Layer-modulated synthesis of uniform tungsten disulfide nanosheet using gas-phase precursors.

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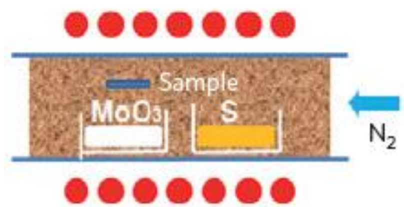
Yonsei University, 262 Seongsanno, Seodaemun-gu,
Seoul, Korea

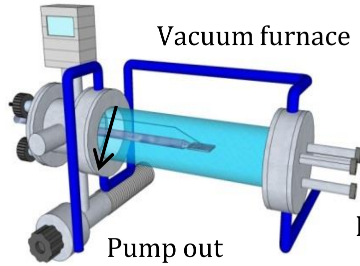
Growth of CVD WS_2

<Previous CVD method>

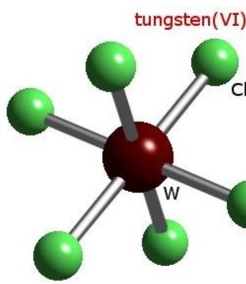


Lee Y-H et al, *Adv. Mater*, 24, 2320–2325, (2012)

<Gas Phase CVD WS_2>



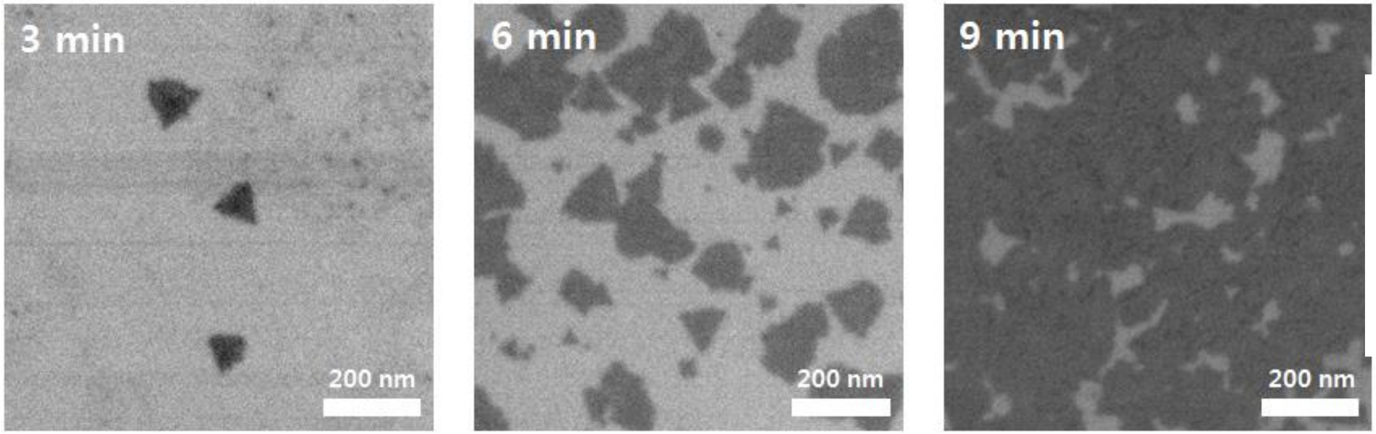
WCl_6



Tube furnace

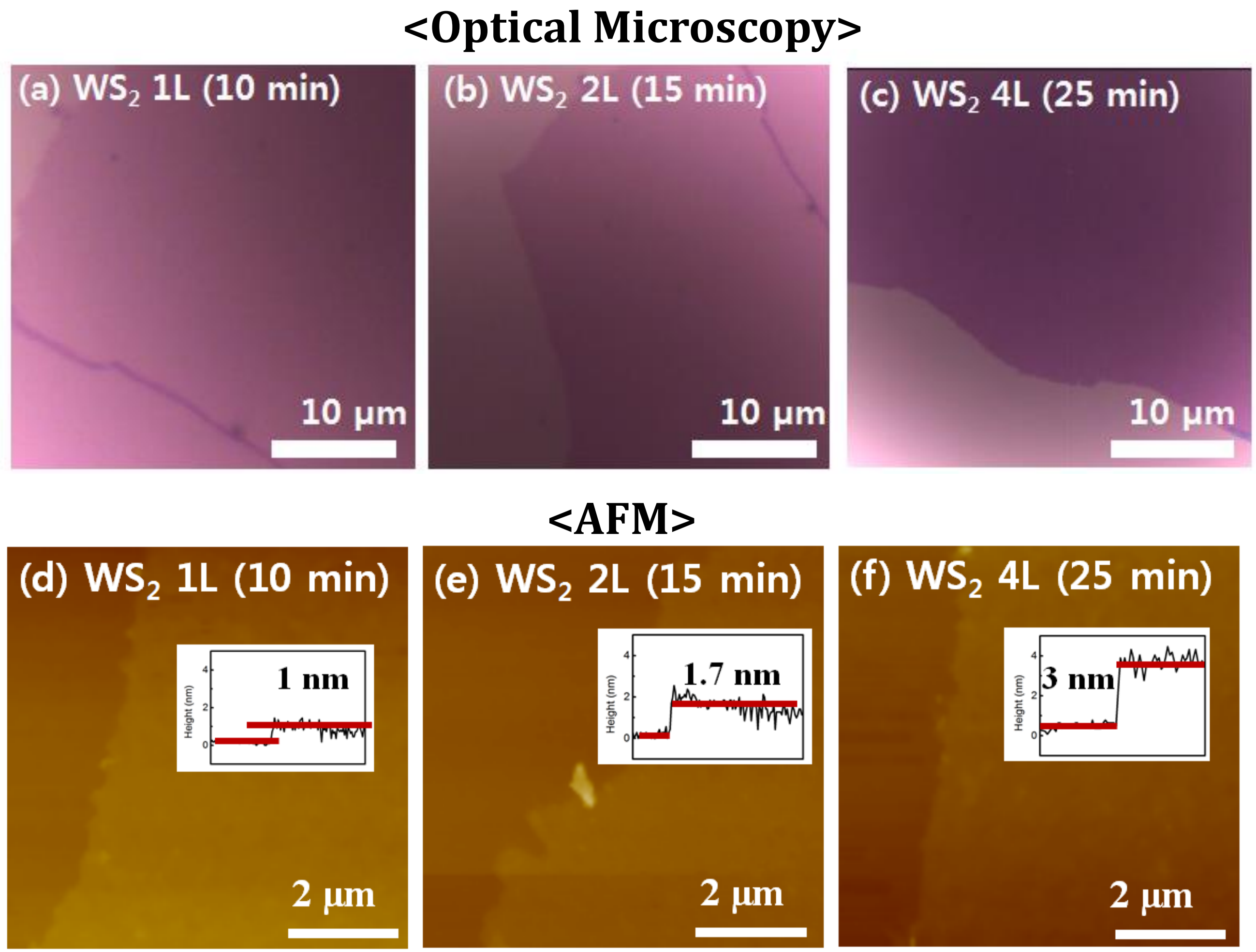
Growth temperature : 700 °C

<SEM>



- Initial growth of CVD WS_2 → Time dependent lateral growth of WS_2

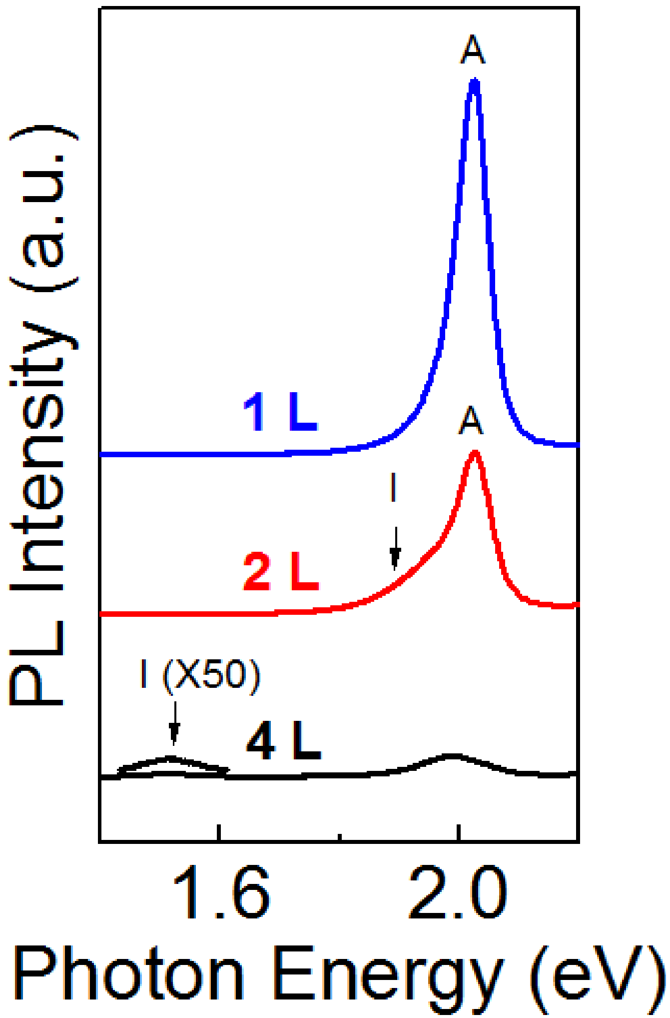
Time dependent Layer Control



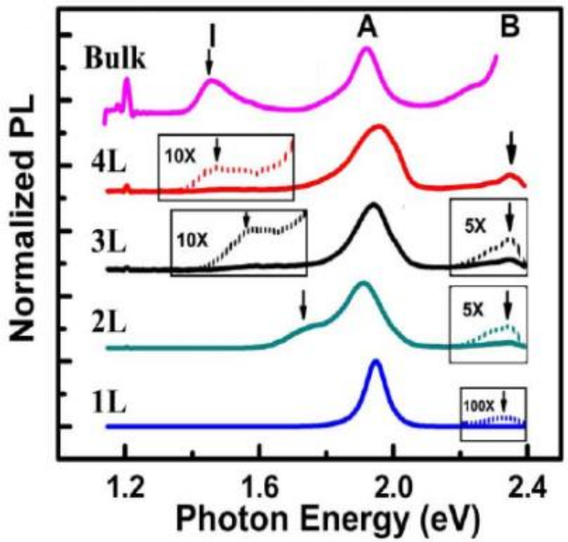
- Number of layer dependent on the cycle number of ALD WO_3

Optical Property of CVD WS_2

<PL>



<Electronic structure of WS_2>



Zeng, H. et al, *Sci, Rep*. 3, 1608, (2013)

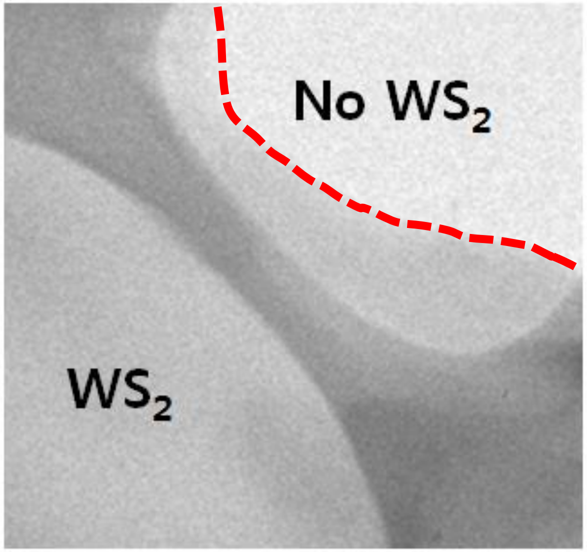
- PL spectra for the 1L, 2L and 4L WS_2 nanosheets

  → Indirect to direct band gap transition with reducing number of layer

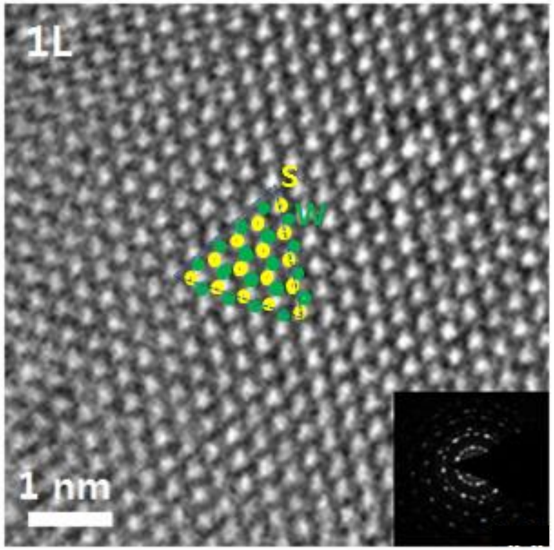
  → I peak from PL spectrum of 2L and 4L WS_2

Atomic Arrangement of CVD WS_2

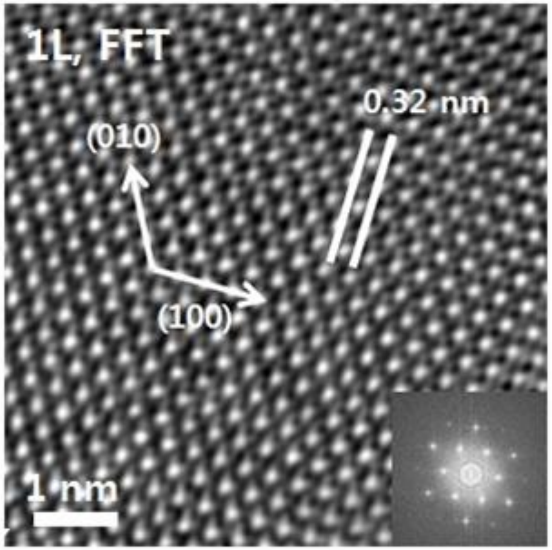
<TEM>



<HRTEM>



<Inversed FFT>

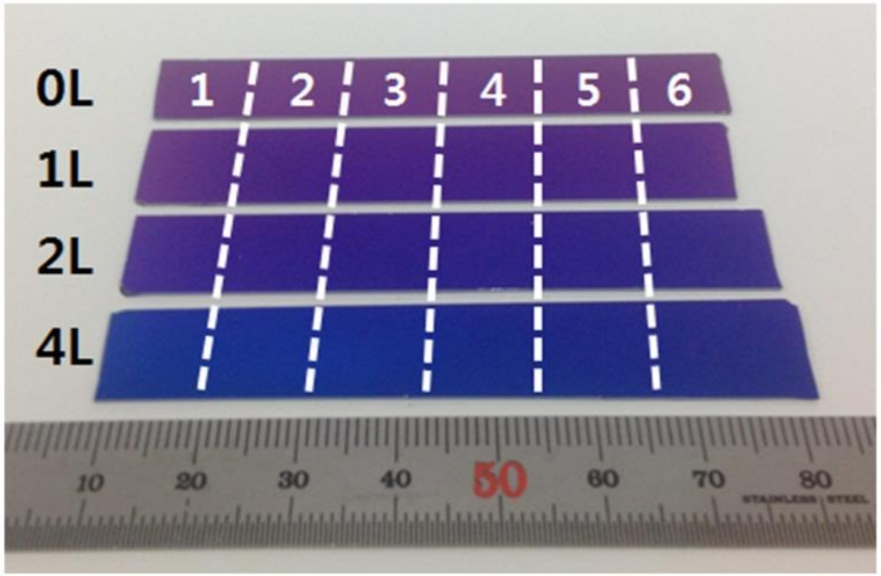


- Low-magnification TEM image for a 1L WS_2 nanosheet on a TEM grid
- HRTEM image of 1L WS_2 nanosheet at a selected region and (inset) the SAED pattern
- Inverse FFT by applying a mask

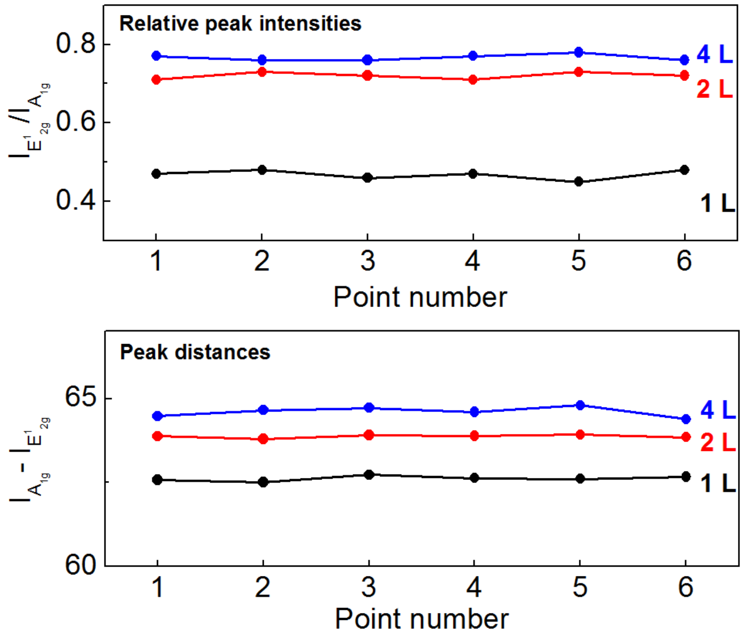
→ (100) and (110) crystal directions

→ Lattice spacing: 0.26 nm and 0.16 nm for the (100) and (110) planes

Large Area Uniformity of CVD WS_2



<Raman analysis>



- Color dependency on the number of layers
- Large-area uniformity on 1 cm X 7 cm SiO_2

Graphene/WS_2 Photo-Detector

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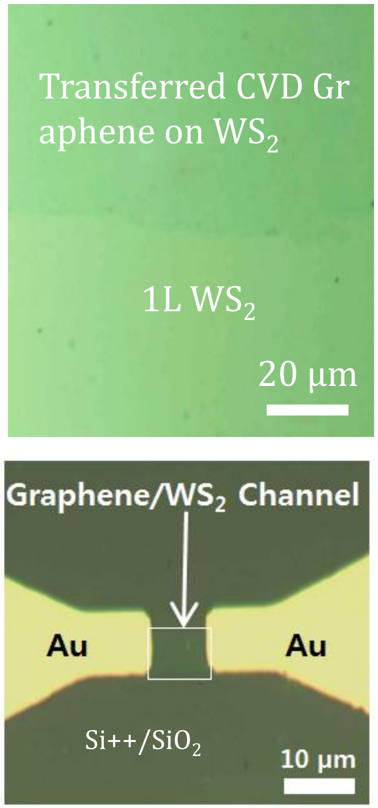
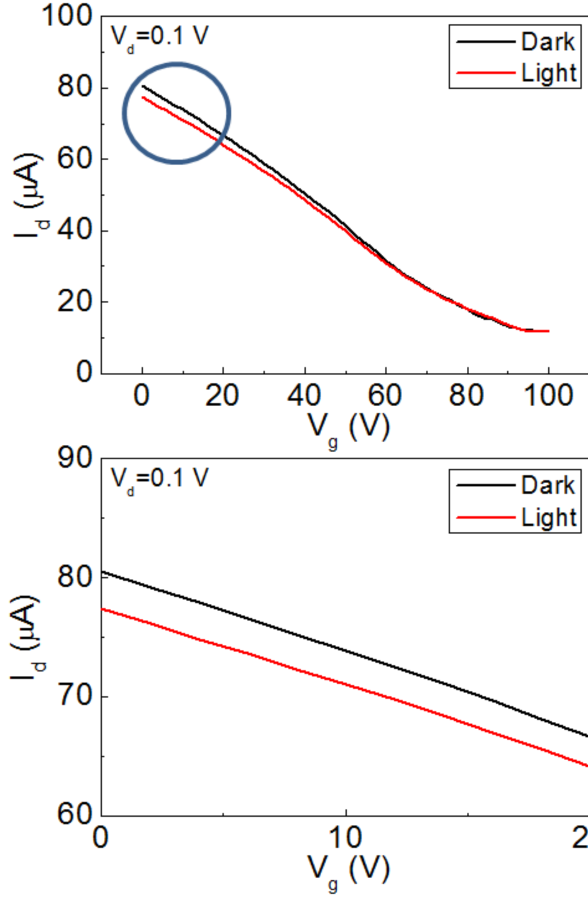
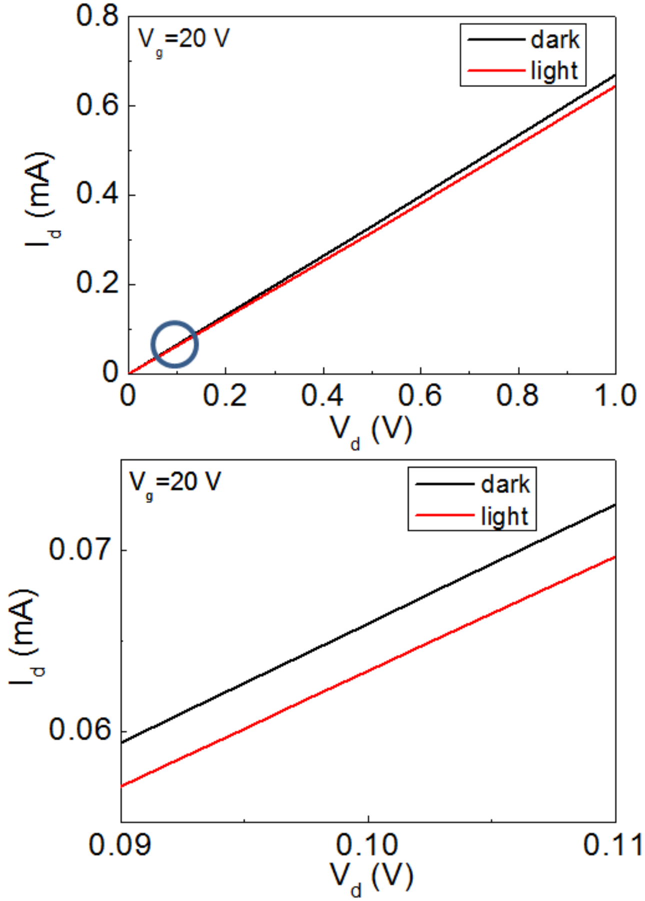


Unpublished Data

<Transfer curve>



<Output curve>

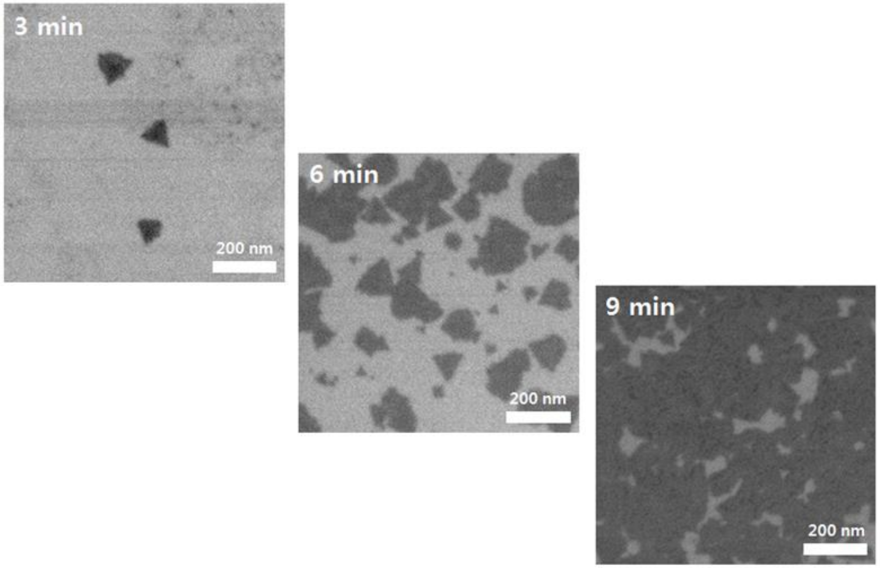


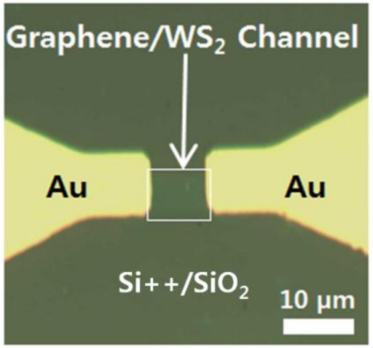
- △Id/Id @ Vg=0 V -> 4% with monochromatic green light (~550 nm) @ 1 W/m^2
- Lower than exfoliated few-layer MoS_2 with CVD graphene photo-detector (~ 7% @ 0.6 W/m^2)

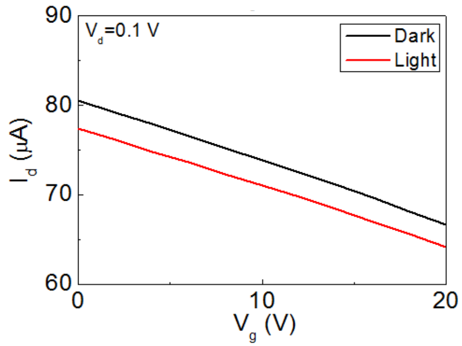
Kallol Roy et al, *Nat nanotech*, 8, 826–830, (2013)

Summary

- CVD WS_2 nanosheets are synthesized using gas phase S reactant
- Lateral growth and coalescence of two or more domains are observed
- Number of layer can be controlled by reaction time





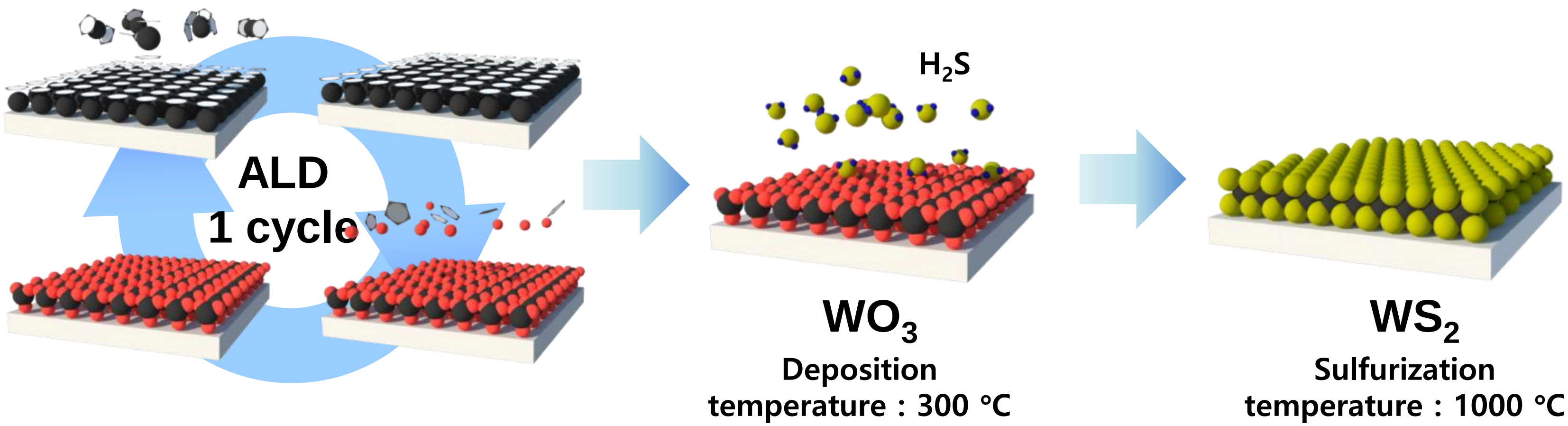


- Graphene/WS_2 hetero-structure shows properties of photo detecting

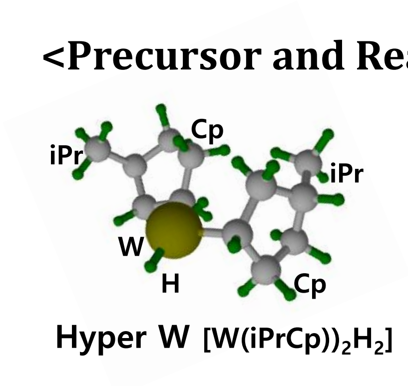
Synthesis of TMDCs nanosheet Based on Atomic Layer Deposition (Metal Oxide Sulfurization)

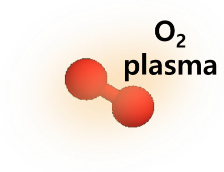
Synthesis of WS_2 Nanosheets Using ALD

<Procedure of ALD based WS_2 nanosheets synthesis>

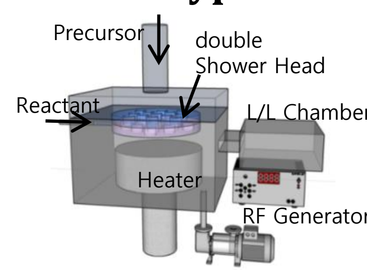


<Precursor and Reactant for ALD WO_3>





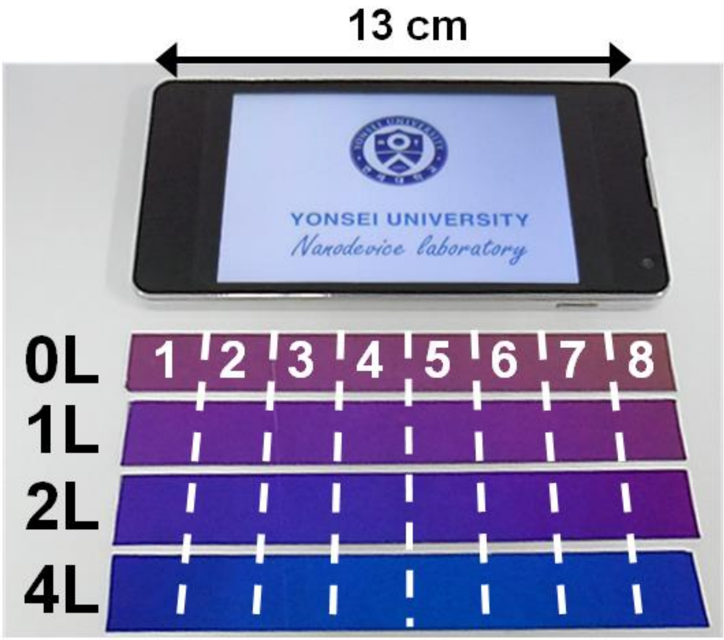
<Shower head type 6 inch ALD>



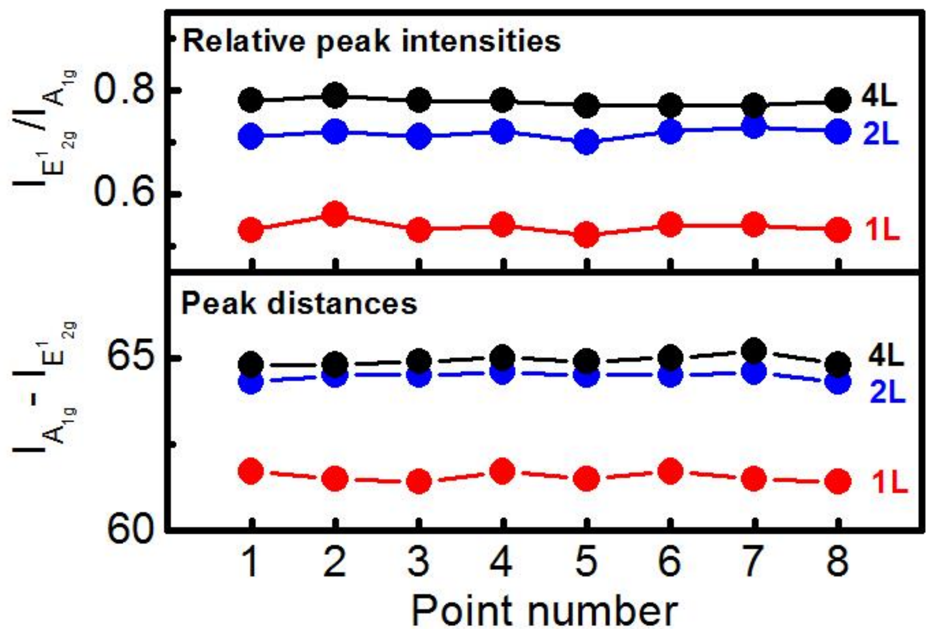
- Hyper W and O_2 plasma as precursor and reactant for ALD WO_3
- Shower head type 6” ALD plasma reactor for ALD WO_3

***ACS Nano*, 7(12), 11333–11340, (2013)**

Wafer-Scale Uniformity of WS_2



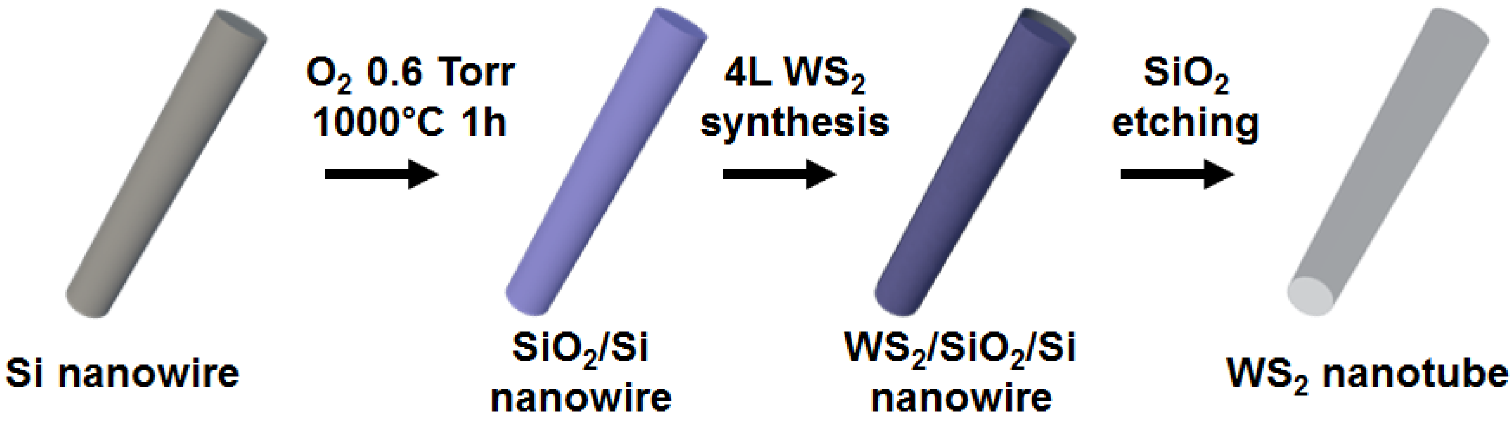
<Raman analysis>



- Large area (approximately 13 cm) 1L, 2L and 4L WS_2 nanosheets
- Relative Raman peak intensities and peak distances of the E^1_{2g} and A_{1g} modes for eight measurement points on large area WS_2 nanosheets

WS_2 Nanotubes Fabrication

<Synthesis procedure of WS_2 nanotubes>



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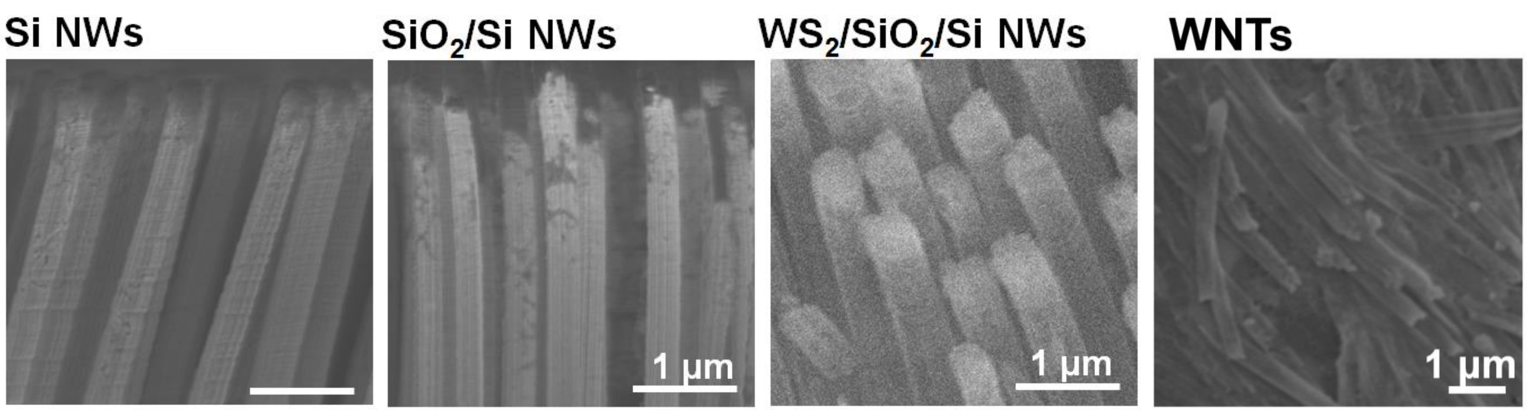
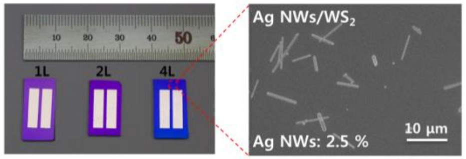


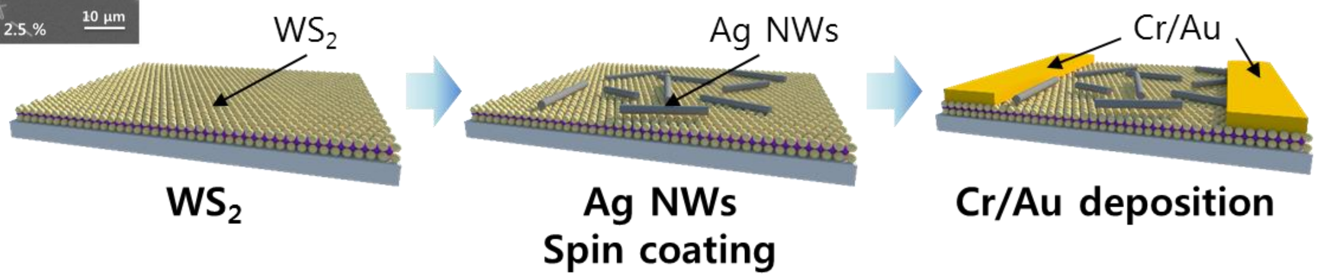
- Conformality of ALD

  → Fabrication of WS_2 nanotubes using ALD based WS_2 proc

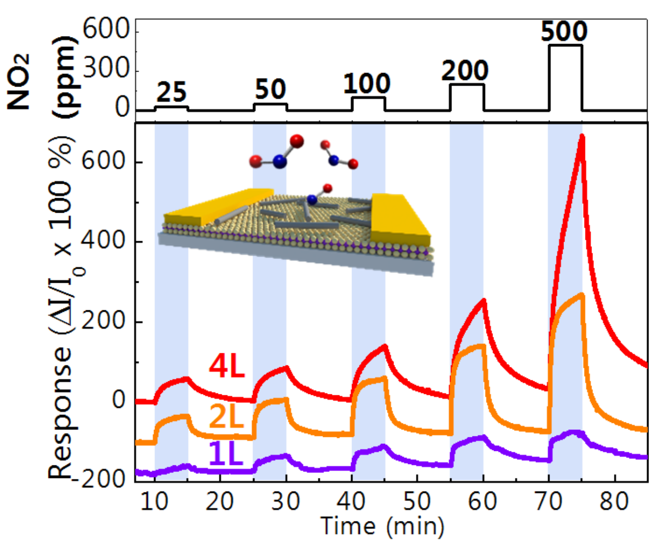
Gas Sensing Properties of WS_2



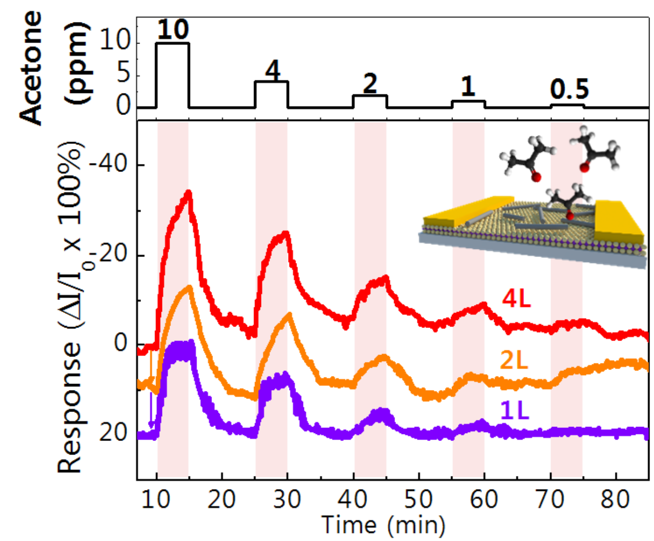
<Functionalization of WS_2>



<NO_2 Gas Sensing>

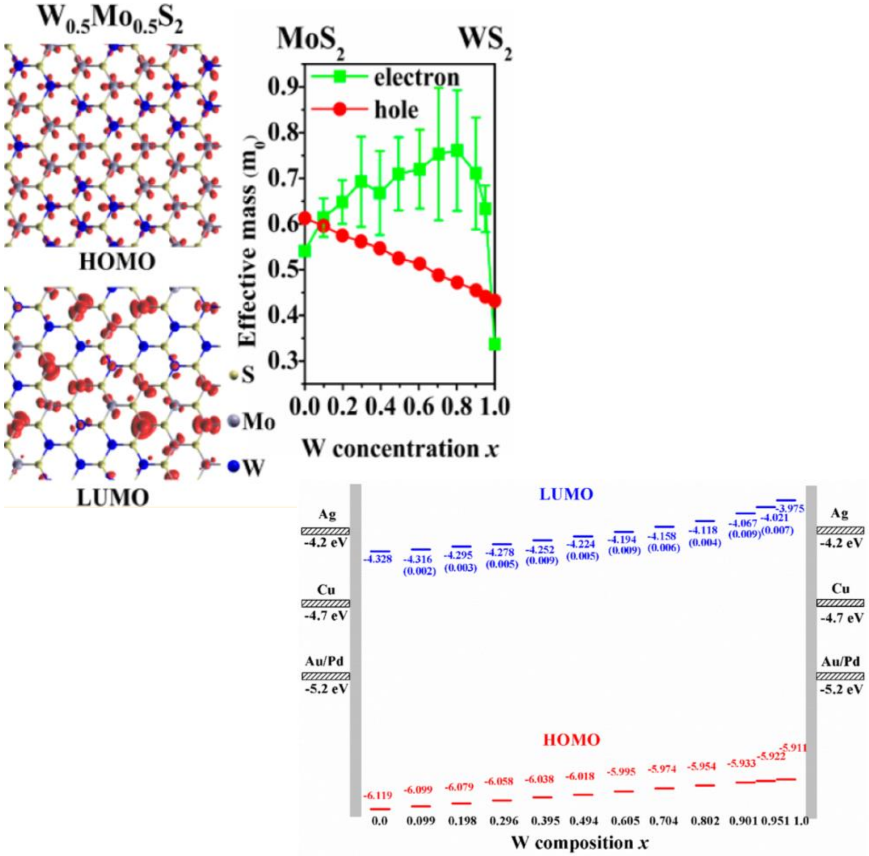


<Acetone Gas Sensing>

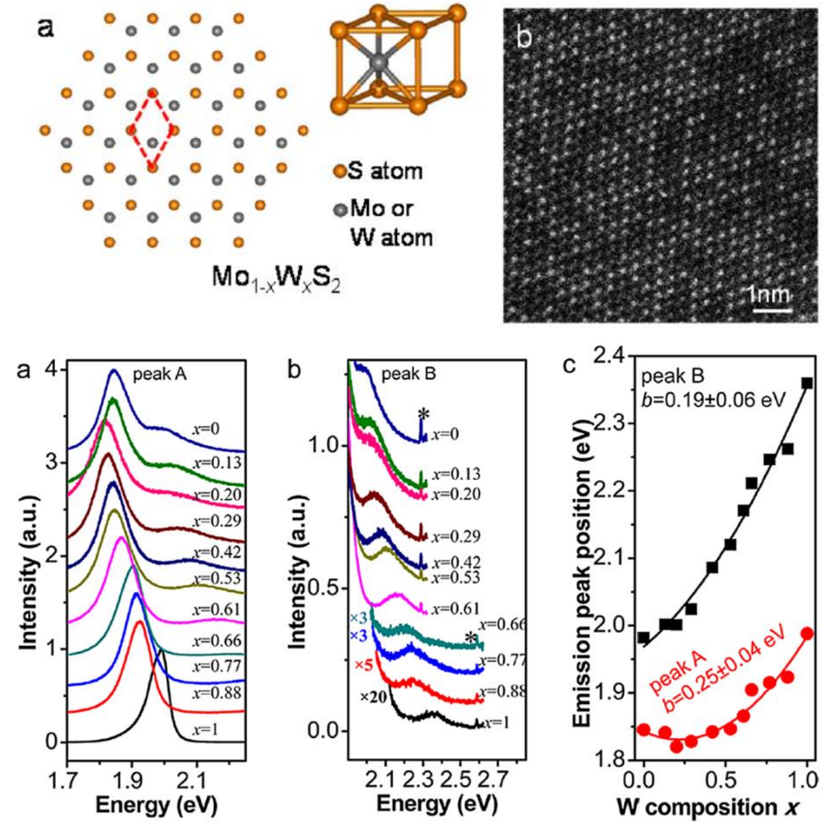


- Highly enhanced response to NO_2 → 12 times enhanced compared to pristine

$Mo_{(1-x)}W_xS_2$ Nanosheets



Jinyang Xi et al, *Jour of Phy. Chem. Lett*, 5, 285–291, (2014)

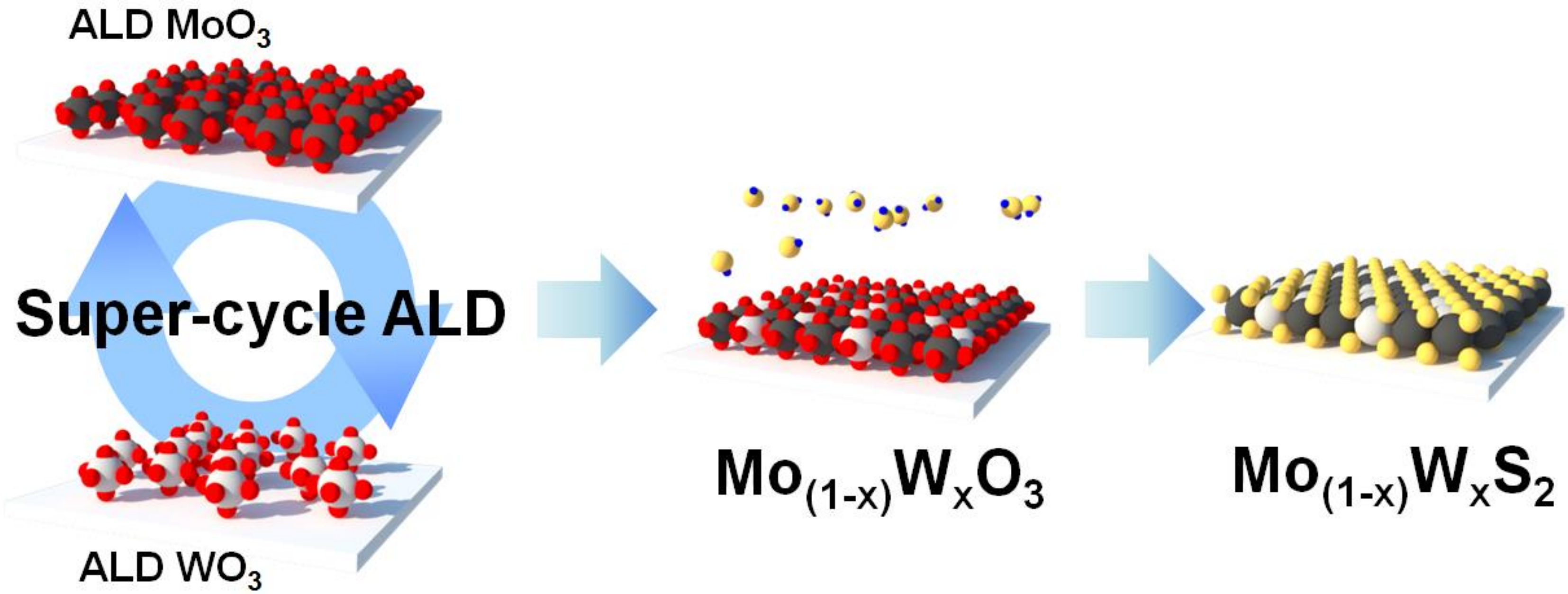


Yanfeng Chen et al, *ACS Nano*, 7(5), 4610–4616, (2013)

- 2D $Mo_{(1-x)}W_xS_2$ nanosheets
  → Thermally stable, tunable band gap with control of composition ratio
- No report on synthesis of 2D $Mo_{(1-x)}W_xS_2$ alloy nanosheet

Synthesis of $Mo_{(1-x)}W_xS_2$ Nanosheets

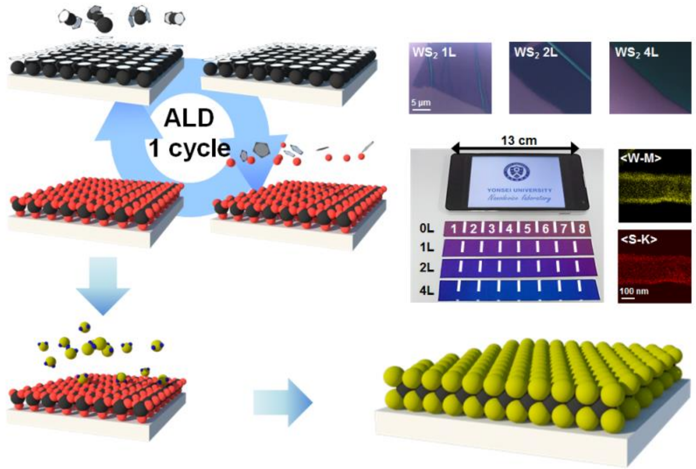
<Synthesis procedure of ALD based $Mo_{(1-x)}W_xS_2$ nanosheets>

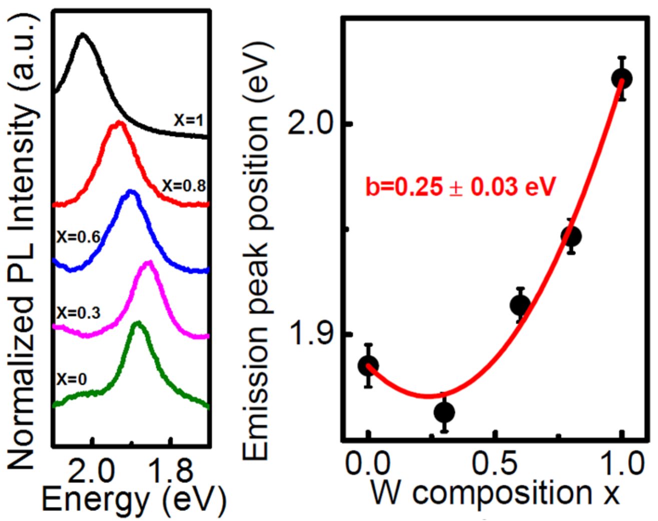


- Sulfurization of $Mo_{(1-x)}W_xO_3$ thin films deposited by super-cycle of PE-ALD
- Depending on the cycle ratio of MoO_3 and WO_3, contents ratio of Mo and W can be controlled

Summary

- ALD based WS_2 nanosheets show several advantages of ALD
  → Atomic scale thickness control,
  → Wafer-scale uniformity,
  → Conformality



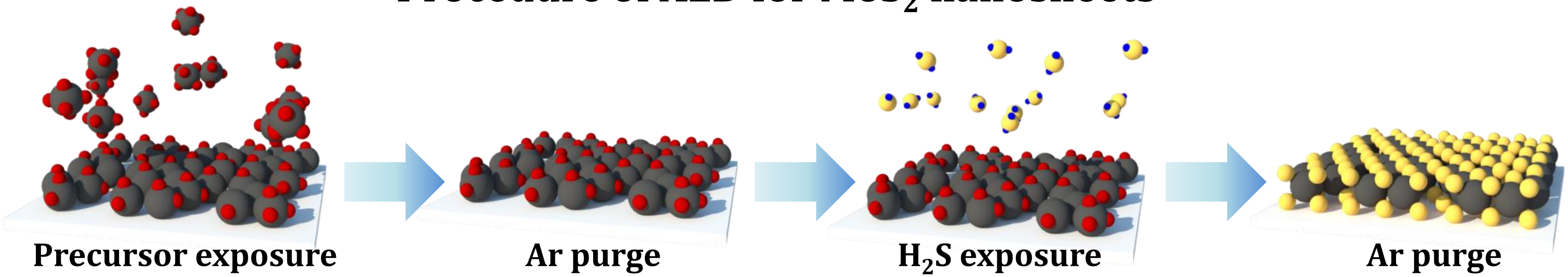


- Super-cycle ALD can be possible tuning of band gap of 2D TMDCs nanosheets by synthesis of $Mo_{(1-x)}W_xS_2$ alloy and vertical composition-controlled $Mo_{(1-x)}W_xS_2$

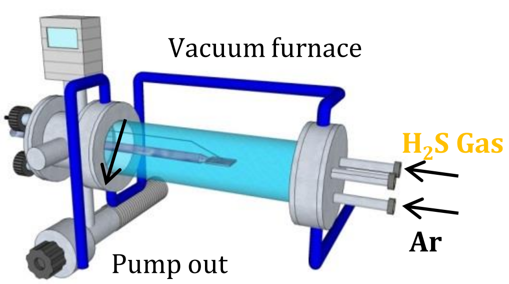
Synthesis of MoS_2 nanosheet Based on Atomic Layer Deposition (Direct Synthesis)

Synthesis of MoS_2 Nanosheets

<Procedure of ALD for MoS_2 nanosheets>

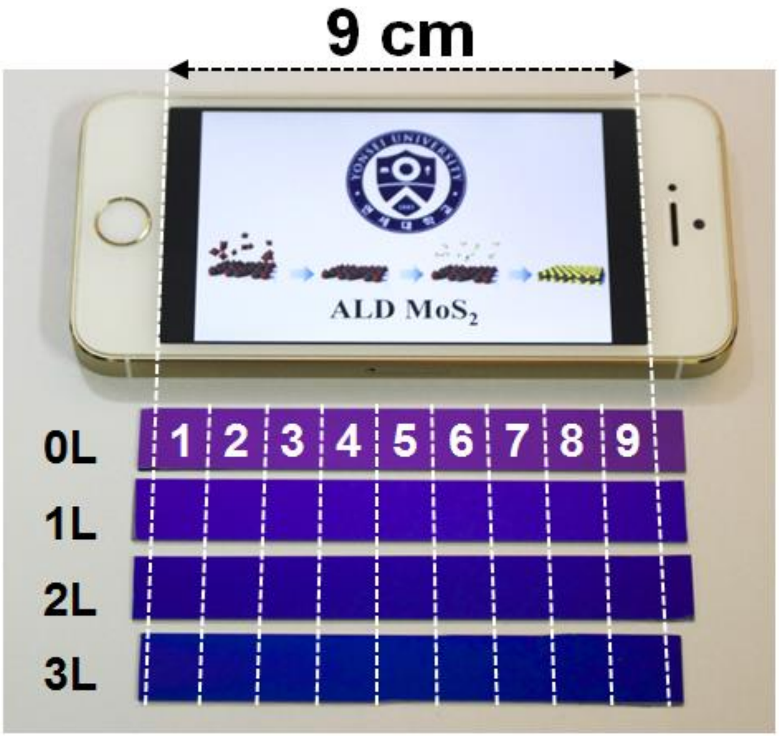


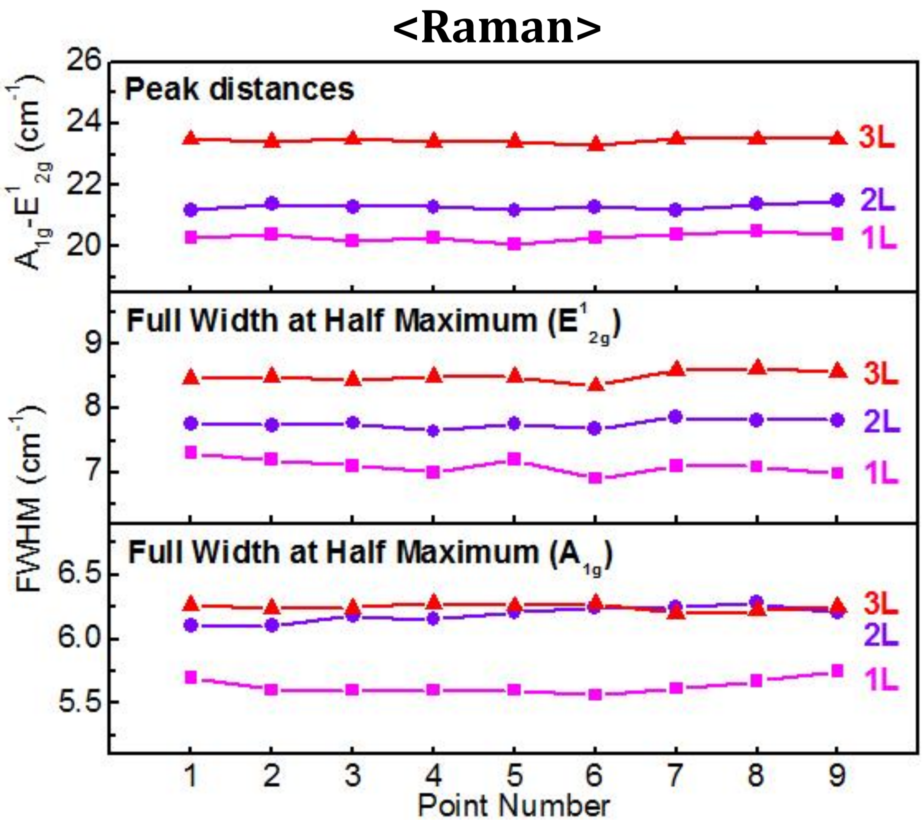
<Equipment for ALD>



- Gas phase H_2S is employed as the reactant in ALD MoS_2 process
- Tube type furnace ALD reactor for MoS_2

Wafer-Scale Uniformity of MoS_2





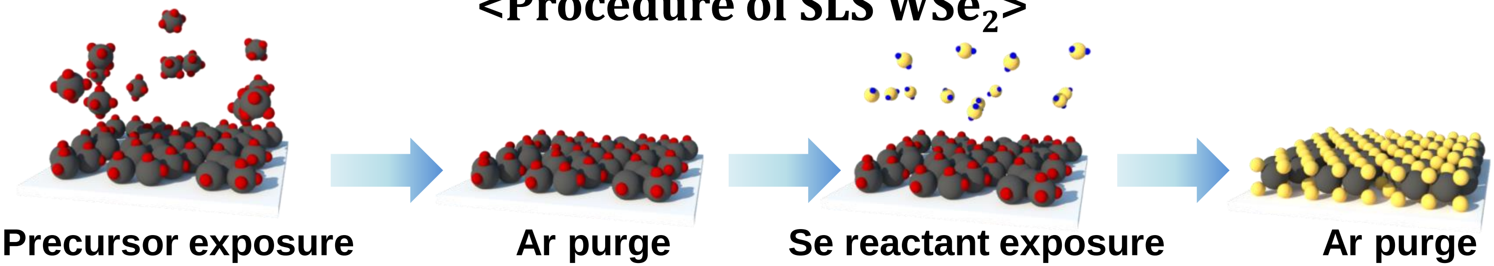
Submitted

- Large area (approximately 9 cm) 1L, 2L and 3L MoS_2 nanosheets
- Relative Raman peak distances and FWHM for E^1_{2g} and A_{1g} modes for nine measurement points on large area MoS_2 nanosheets
- Results show small variation for the nine points

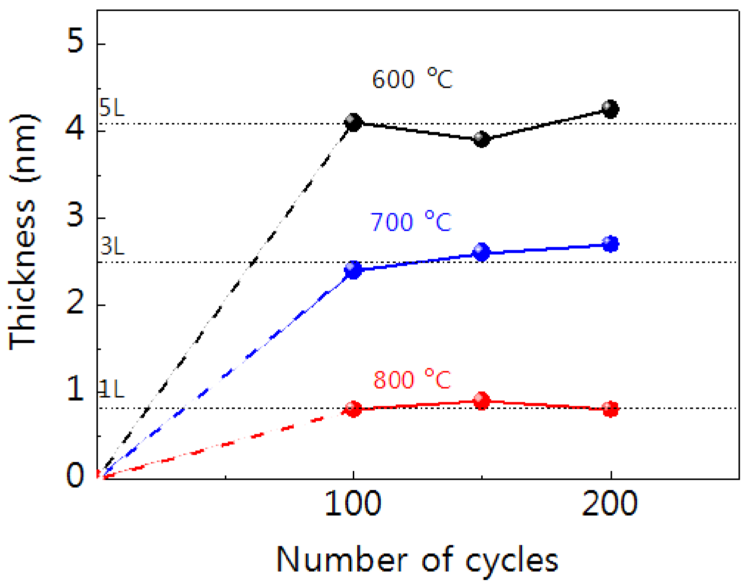
→ good thickness uniformity over wafer-scale

SLS WSe_2

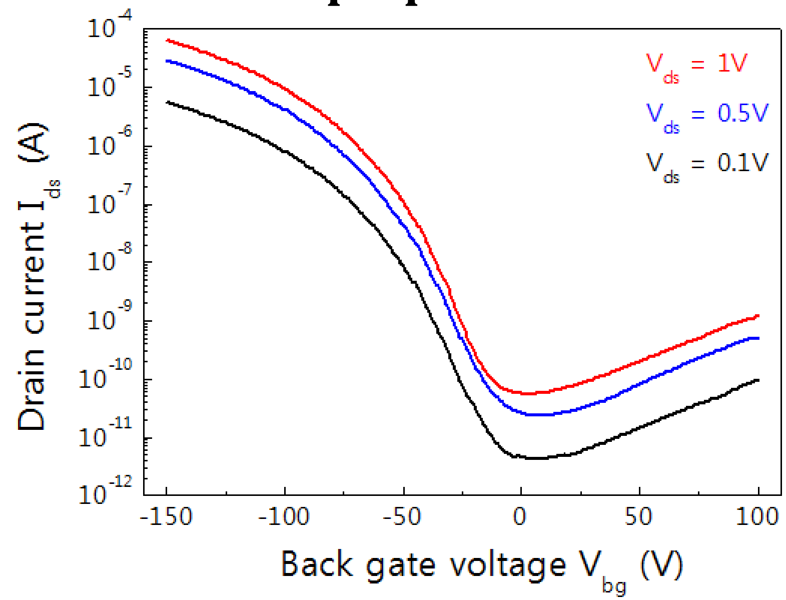
<Procedure of SLS WSe_2>



<Self-limiting Layer Synthesis>

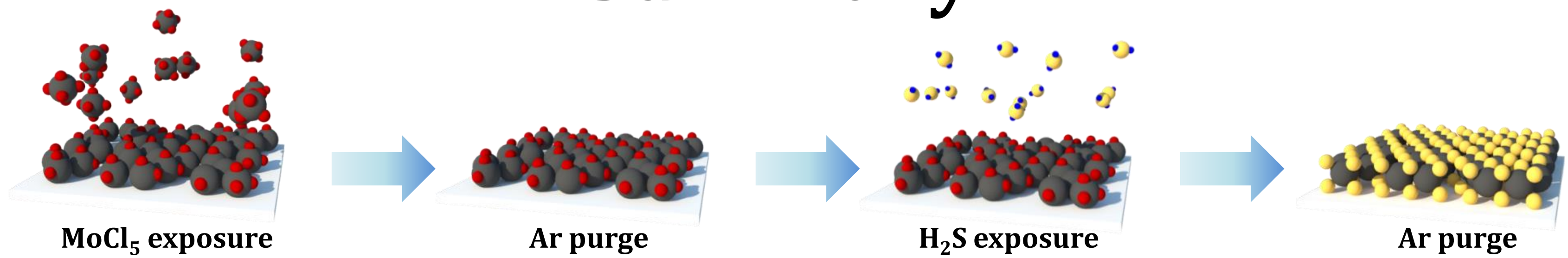


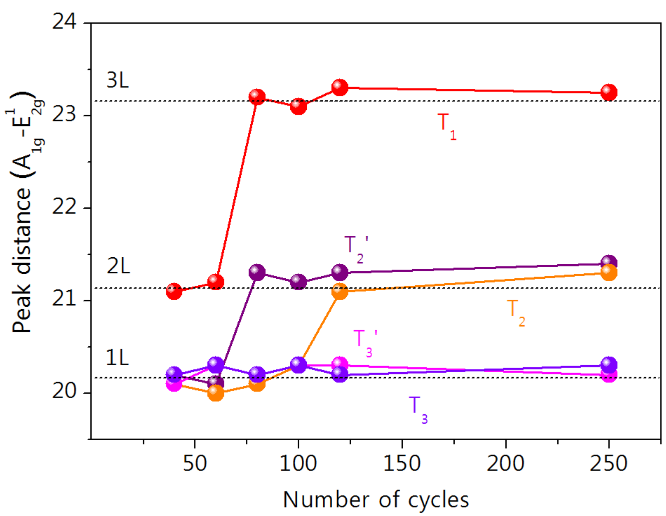
<Electrical properties of 3L WSe_2>

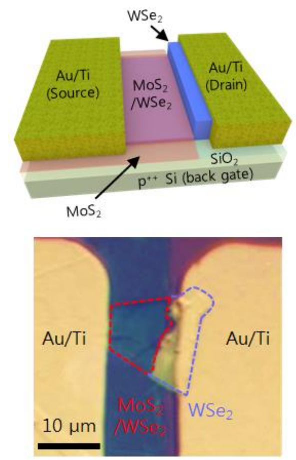


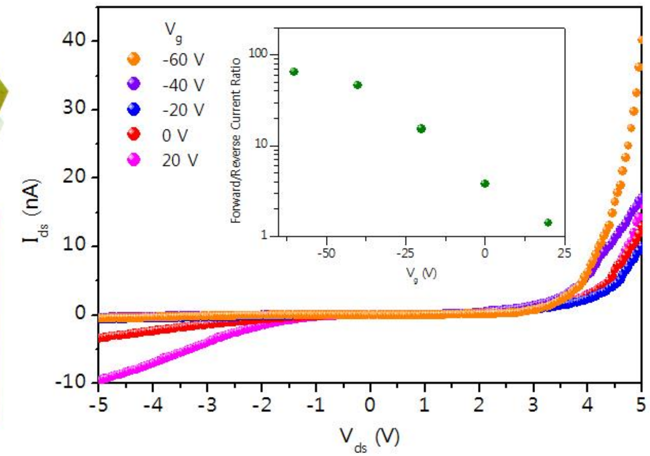
- Preserving self-limiting layer synthesis characteristics for WSe_2
  → Universally applicable to synthesize 2D TMDCs
- 3L WSe_2 → p-type behavior with mobility = 2.2 cm^2/Vs, on/off ratio = 10^6

Summary









- Synthesis of MoS_2 nanosheet using ALD procedure

  → Show self-limiting growth behavior (self-limiting layer synthesis, SLS)
- SLS MoS_2 shows wafer-scale thickness uniformity and layer controllability
- SLS MoS_2 valid on WSe_2 surface → feasible for 2D TMDCs heterostructure